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INVESTIGATIONS ON LIGHT AND HEAT, made and published wholly or in part with appropriation from the RUMFORD FUND.

XI.

DISTRIBUTION OF HEAT IN THE SPECTRA OF
VARIOUS SOURCES OF RADIATION.

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THE following research has had for its object a study of the distribution of heat in the spectra of a variety of substances, each heated to various temperatures.

Experiments upon the distribution of heat in the sun's spectrum have already been made by a large number of experimenters, and a few have measured the heat from some terrestrial sources. The former class have failed to give us much scientific information, both because we know so little about our source of radiation, and because we are so little able to estimate the absorbing effect of our atmosphere upon the rays that are given out. The latter class have been too limited, and they are too little comparable with each other. In all of them there may be detected very considerable errors. In fact, the experiments that have thus far been made have hardly more than served to guide us in selecting the best methods and apparatus for further research, and to point out the more important sources of error.

In this research the author has made use of such results as the various experimenters upon the distribution of heat in the spectrum, from the time of Sir W. Herschel down to the present day, have obtained; and, profiting by them, has attempted to advance the method one step further, and to determine some relations between the quantitative structure of various substances and the distribution of energy in their spectra, as well as the effects of varying temperature, of liquefaction, and of chemical change of a source of radiation, upon the kind of rays it gives out.

The experiments have included a measurement of the distribution of heat in the spectrum of a platinum wire, heated to various measured temperatures between a low red and a full white heat, which resulted in the discovery that platinum gives a spectrum in which the relative distribution of energy is nearly the same for all temperatures between these limits.

That is, if we represent the intensities of heat at different parts of the spectrum by ordinates, the curve joining these will have nearly the same geometrical form, and the same position of the maximum, for all temperatures of the wire between these limits. The curve of distribution was then determined at a low red heat, at a bright red, and at a white heat for the black oxide of copper (CuO), the black oxide of iron (Fe_3O_4), the red oxide of iron (Fe_2O_3), the green oxide of chromium (Cr_2O_3), and the white oxide of aluminium (Al_2O_3).

It was found that for each substance the geometrical form of the curve was nearly independent of the temperature, but that it varied somewhat with the different substances.

A relation between the molecular weights of these substances and the forms of the curves, and also a relation between the colors of the bodies at the ordinary temperatures and the radiations emitted when heated, appeared in a study of their curves. The effect of the passage from the solid to the liquid state was studied in the case of CuO , and it was found that the geometrical form of the curve remained the same.

The present paper contains a review of the more important experiments that have been made upon this subject, and to these there is added an account of the author's own experiments.

HISTORICAL.

Previous to the time of Sir Wm. Herschel there had been no really scientific study of the distribution of heat in the spectrum.

As the results of three very limited and inaccurate series of experiments, by Landriani,* Rochon,† and Senebier,‡ it was supposed that the sun's rays of light were accompanied by rays of heat, which were in general stronger for rays of low than for those of high refrangibility, but which reached their maximum somewhere in the yellow or orange rays.

* Ann. der Physik, x.

† Recueil de Mém. sur la Méc. et Physique, 1783.

‡ Mem. Physico-chimiques, ii. 74.

In 1800 Sir Wm. Herschel published in the *Philosophical Transactions* a series of experiments on this subject, which were, without doubt, as accurate as the means at his command would allow, and which later experiments have amply confirmed.

He allowed the spectrum formed by the passage of the sun's rays through a glass prism to fall upon a screen, in which there was a slit, which could be moved to different parts of the spectrum. Behind this slit he placed a very sensitive thermometer, and, moving the slit through the spectrum, found that, after successive exposures of ten minutes each, it rose in the violet $1^{\circ}.1$; in the green, $1^{\circ}.8$; in the red, $3^{\circ}.8$. Moving the slit still farther and beyond the limits of the luminous spectrum, he found that on the very border of luminosity the thermometer stood at $3^{\circ}.6$, and even at a distance of five centimeters from this point the reading was $1^{\circ}.7$. In the ultra-violet there was no effect.

The field having thus been opened, various experimenters took up the subject, in order to find the form of the curve of distribution, and the position of maximum heating effect.

Leslie,* in repeating Herschel's experiments with what he claimed to be a delicate differential thermometer, found, as the experimenters previous to Herschel had, that the maximum was within the luminous spectrum, and, in a somewhat severe criticism of Herschel's work, attributed his results to the heating of the inclined plane on which the thermometers were placed.

Mickle,† in experimenting on the subject, found that the prism itself became somewhat heated, and concluded that Herschel's apparently anomalous results were due to radiations from the prism.

Englefield‡ found, as Herschel had done, that the maximum was in the ultra-red.

An accurate series of experiments carried out by Wünsch,§ and a perhaps still more praiseworthy series, which tended only to confirm the first, made by Seebeck,|| showed that the form of the curve and the position of the maximum was largely dependent upon the material of the prism used, and that Herschel's results were, for the kind of glass used, entirely correct.

In 1833 Melloni ¶ published in the *Ann. de Chimie et de Physique* the results of a very accurate and extended series of experiments on

* Nich. Journ., iv.

† Journ. Roy. Inst., 1802.

‡ Abhandl. d. Berl. Akad., 1819.

† Phil. Mag., lxx.

§ Gehler's Journ., vi.

¶ Ann. de Chimie, liii.

the radiation of heat, in which his measurements were made with the thermopile instead of mercury thermometers.

These researches included a study, made with this instrument, of the distribution of heat in the spectrum. He found, as Wünsch and Seebeck had done, that the distribution of heat was dependent upon the material of the prism used, and that the reason why different substances gave different spectra was because each possessed an absorptive power for certain of the heat rays. The selective absorption of some substances gave rise to sinuosities in the curve of distribution.

There was one substance, however, that he found to be transparent for all rays, both of light and heat. This was rock-salt. Fluor-spar he found to be the nearest to approach it in diathermacy. Resuming the study of the spectrum with prisms of rock-salt and the thermopile, he found the maximum to be at a distance beyond the red equal to the distance of the yellow from the same.

In the Philosophical Transactions for 1840, Sir John Herschel published the results of a series of measurements of the distribution of heat in the spectrum, made by exposing to its rays a thin blackened paper, which had been covered with some easily evaporated liquid. The points of greatest intensity of heat showed themselves by the greatest evaporation of the liquid. His results were, in general, similar to those previously obtained, but, in addition, he claimed to have discovered lines of discontinuity, similar to the Fraunhofer lines of the luminous spectrum.

Melloni, in the *Comptes Rendus** for the same year, criticises the results obtained by Herschel, and says that they cannot be regarded as an accurate measurement of the distribution of heat, because the blackened paper would not absorb all the rays in the same proportion, and because its conductivity would extend the evaporation at points of great to those of low intensity. The lines of discontinuity he claims to have discovered himself, and to have explained by the selective absorption of the prism.

In 1858 a research upon the distribution of heat in the sun's spectrum was made by J. Müller.† He used prisms of rock-salt and of glass for obtaining the spectra, and a carefully constructed thermopile and galvanometer for estimating the temperatures. His experiments included a study of the effects of interposing various colored solutions in the paths of the rays, and, later, studies of the effects of using different prisms. With regard to the position of the

* T. xi.

† Pogg. Ann., cv.

maximum, his conclusions were substantially the same as those of Melloni.

In addition, he made some estimates of the wave-lengths of the dark parts of the spectrum by means of an empirical formula, derived from measurements in the luminous spectrum. As a result of these calculations, he found the wave-length of the limit of the dark spectrum to be 0.00183^{mm} . He admits, however, that this value is very inexact, and we shall see further on that it can hardly be considered an approximation, both because the method is so crude, and because the limit of the spectrum cannot be fixed.

Dissatisfied with his results, he experimented upon the spectrum from a diffraction grating, in which the elongation of the spectrum is proportional to the wave-length.

Similar experiments had already been made by Draper,* who stated as the result of his observations that the distribution of heat corresponded to the distribution of light and reached its maximum in the yellow.

Draper's experiments were made with somewhat crude and not very delicate apparatus, and Müller, in repeating them with a much more sensitive thermopile, found, as Draper had done, that the maximum of the diffraction spectrum fell in the yellow, but he did not find the intensities of heat proportional to the light.

The curve of distribution which he obtained rose very steeply from the violet to the yellow, and then fell gradually and became insensible at a point distant from the red equal to three and one half times the length of the luminous spectrum.

The reason of the non-coincidence of intensity of the luminous and thermal spectra had been sought by Melloni† (who thought it was due to a coloration of the crystalline lens), and by Brücke,‡ Cima, Tyndall, and Jansen.

But the most complete research seems to have been carried out by Franz,§ who published an article upon the diathermacy of the media of the eye in 1862. In these experiments, he interposed the various media of the eye, placed between plates of rock-salt, in the path of the rays, which were afterward dispersed by a rock-salt prism, and found that the humors of the eye all absorb the ultra-red rays very largely, and the luminous rays to a much smaller extent.

He also showed, by measuring the distribution of heat in the sun's

* Phil. Mag., 1857, xiii. 153.

† Pogg. Ann., lxv. and lxix.

‡ Pogg. Ann., lvi.

§ Pogg. Ann., cxv.

spectrum on days of different degrees of clearness, and at different seasons of the year, that the watery vapor absorbed the non-luminous rays so largely, and in so different a proportion to the absorption of the luminous rays, that on two days in August, only nine days apart, the non-luminous spectrum extended, in one case, only as far beyond the red as the green was on the other side, and, in the other, a distance equal to the luminous spectrum. He concluded, from his observations, that it is not possible to make quantitative studies, if the sun be used as a source of light, nor if the eye be used in measurements.

Knoblauch* published in 1863 the results of a series of experiments upon the transmission of radiant heat through rock-salt, in which he studied the effects upon the distribution of heat in the spectrum. He concluded from his experiments, that prisms of chemically pure rock-salt allowed rays of heat of all kinds to pass through in equal proportions; that the maximum of the solar spectrum found by such a prism fell outside the red, and that the distribution of heat for the luminous part of the spectrum is the same for prisms of rock-salt and of glass.

Cloudy rock-salt, however, he found, interrupted rays from the sun more than from an Argand burner, and rays from this burner more than from a source heated to 100° C.; and also that chemically or mechanically impure rock-salt diffused the light and exercised a selective absorption. He obtained, also, many other results, which are not, however, of special interest here.

The next experimenter in this field was Desainés,† who used, as a source of heat, pieces of lime and platinum heated to incandescence in a lamp. The prism used was of rock-salt. He found that the maximum was beyond the red rays, and that water absorbed the ultra-red. Comparing the spectrum from platinum with that from the sun, he found that, while the maximum for platinum was 1.15° from the line of no dispersion, for the sun it was 0.46° at 8 A.M., and 0.51° at noon.

Lamansky‡ explored the sun's spectrum with a very narrow thermopile, and found in the ultra-red spectrum places of low heat, which he says are similar to the Fraunhofer lines of the luminous spectrum. But these, as we have seen, had already been noticed by Herschel, and were attributed by Melloni to the absorption of the prism.

Lamansky, however, finds that, so long as the sun is used as a source of heat, these lines appear the same for a prism of bisulphide of car-

* Pogg. Ann., cxx.

† Comptes Rendus, lxx.

‡ Pogg. Ann., cxlvi.

bon as for one of rock-salt, and that when the calcium light was substituted for the sun they entirely disappeared. These lines, he found, were in groups, each of which was quite broad. The index of refraction of the farthest group he estimated at 1.5274.

There are two other series of experiments, brief notices of which seem to be necessary for the completion of the history of the subject. That of Tyndall* on the distribution of heat in the spectrum of the electric light; and that of Draper,† in which he compares the heat of equivalent parts of the spectrum.

The experiments of Professor Tyndall were made with exceptionally fine apparatus, and undoubtedly represent the distribution from the electric light with considerable accuracy. The curve he obtains is somewhat symmetrical about its point of maximum, and this maximum is found at a distance beyond the red about equal to the distance on the other side of the green. The total length of the invisible spectrum measured was about *twice* that of the visible. The ordinates near this point of maximum he found to be very much greater, compared with those of the luminous spectrum, than those found by other experimenters. He also experimented upon the effect of introducing water and various other media in the path of the rays, with results essentially similar to those we have already seen.

Professor Draper, in his paper, calls attention to the fact, that in the prismatic spectrum the length of any part is not, as in the diffraction spectrum, proportional to the differences in wave-length of its extremes, but is more and more condensed as we go from the violet to the red.

He supposes this to be the reason of the apparent increase of thermal effect, and shows, by an extended series of experiments, that the amount of heat between the *A* line, for which $\lambda = 7604$, and the point for which $\lambda = 5768$, when converged by a concave mirror upon a thermopile, had nearly the same heating effect as the portion between $\lambda = 5768$ and the H_2 line, for which $\lambda = 3933$; $\lambda = 5768$ being the mean of the other two wave-lengths, and called by him the optical centre.

From this, he says, "it necessarily follows that in the spectrum any two equivalent series of undulations will have the same heating power, no matter what their actual wave-length may be." A conclusion, however, which we shall see is by no means correct.

* Phil. Trans., 1866.

† Am. Jour. Sci., 1872.

In the above historical sketch I have tried to represent, as fairly as possible, what has been done in the way of measuring the distribution of heat in the spectrum. Some of the results are undoubtedly quite wrong, and nearly all of them contain very considerable errors; but the experiment is a delicate one, and the results are peculiarly liable to modification from disturbing causes. The results often vary very widely, even when obtained by eminent observers and with excellent apparatus; the reason being that the unknown conditions of the problem have been so different.

Though so large a number of researches have been undertaken, they have all been entirely qualitative. The source of radiation, the dispersing medium, and the means of measuring the heat in the spectrum, have been varied, and the qualitative effects noticed.

The following research has been undertaken with a view to determining the quantitative relations that may exist between the nature and the temperature of the source of radiation, on the one hand, and the geometrical form of the curve of distribution, on the other. A long and laborious series of preliminary experiments was made, in addition to a study of those of other experimenters, in order to determine the nature and magnitude of the disturbing causes. A few of these may, perhaps, be best referred to here, but the larger number will appear in an examination of the apparatus, in which the preventive means also appear.

The first difficulty is, of course, the absorption exercised by the rock-salt lens and prism. Although chemically pure and perfectly cloudless rock-salt has so little selective absorption as to make it an unimportant factor in these researches, the slightest deposition of moisture, or the slightest cloudiness of the material, will exercise a very decided influence. A deposition of moisture, not noticeable to the eye, may form a slight coating of brine that will quite materially alter the form of the curve.

This was a serious cause of error in my preliminary experiments, and undoubtedly has considerably interfered with other experimenters' results. To prevent this, cloudless rock-salt was chosen in the first place, and carefully polished with oxide of tin and alcohol before using. It was afterwards always kept in a perfectly dry atmosphere, secured by means described later.

The selective absorption of the thermopile was guarded against by covering the face with carefully deposited camphor-black,—the selective absorption of which must be too small to enter as a factor here,—

and using the same coating through all the experiments ; so that such error as may have been introduced only entered in its differences.

The superposition upon the spectrum of the reflection from the back of the prism causes a considerable error. This was cut off by a screen of card-board.

There is another source of error, pointed out to me by Dr. Hastings, which fortunately was sufficiently small to be neglected here, but which may prove to be of considerable magnitude in differently arranged or in more delicate experiments.

If the prism be, as is usually the case, and as was the case in these experiments, one having equal angles, the part of the ray interiorly reflected from the second surface upon which the light strikes will be reflected again from the back and from the first side of the prism, and when it comes out of the prism will form an undispersed image superimposed upon the spectrum.

If the two angles at the back of the prism be denoted by β and γ , we have as follows :

$$\begin{aligned} \text{Deviation after first interior reflection} &= \theta = \pi - 2i \\ \text{" " second " " } &= \theta_1 = \pi - 2i_1 \\ \text{" " third " " } &= \theta_{11} = \pi - 2i_{11} \end{aligned}$$

$$\text{Total deviation} = \Delta = \Sigma \theta = 3\pi - 2\Sigma i$$

$$\text{Suppose} \quad i = \frac{\pi}{2} - \beta + \theta,$$

$$\text{then} \quad i_1 = 2\beta - \frac{\pi}{2} - \theta,$$

$$\text{and} \quad i_{11} = \gamma - 2\beta + \frac{\pi}{2} + \theta$$

$$\Sigma i = \frac{\pi}{2} - \beta + \gamma + \theta$$

$$\Delta = 2\pi - 2(\beta - \gamma) - 2\theta.$$

Suppose $\beta = \gamma$, and $\theta = 0$, then $\Delta = 2\pi$, that is, an image of the slit is formed on the screen at a point where the ray has minimum deviation.

For a ray of different refrangibility

$$i = \frac{\pi}{2} - \left\{ \beta = \gamma \right\} \pm \theta,$$

and

$$\Delta = 2\pi \mp 2\theta.$$

Hence an image formed by two refractions and three internal reflections is undispersed.

If the index of refraction $= n = 1.54$, from Fresnel's formulæ, we have the intensity of the image about $\frac{1}{800}$ of the whole prismatic image.

If now the area of the curve be greatly larger than the width of the thermopile slit \times maximum ordinate, this superimposed image may be a considerable cause of error.

The measured spectrum extended over about 140^{mm} , but the ordinates were comparatively very small, excepting over about 50^{mm} ; so that the curve may be considered very nearly equivalent to a triangle, with altitude h (maximum ordinate), base 50^{mm} , and the area $25 h^{\text{mm}}$.

The width of the slit was about 5^{mm} , and we have $5 h^{\text{mm}}$ to compare with $25 h^{\text{mm}}$, or a quotient of $\frac{1}{5}$ which is contained in the $\frac{1}{800}$ times, i. e. there would be an error of about 1%.

This, however, is within the limits of probable error, and as the image always fell near the maximum ordinate, it was never noticed in the experiments. Besides these causes of error there was, at first, trouble on account of diffuse radiation from the source, heating, and consequent radiation from the prism, radiation from surrounding objects, change of temperature of pile, variations of temperature of the source due to air currents, heating of bodies near the source, moisture of the air, and many disturbances of the galvanometer used with the pile, due to change of sensitiveness of the needles and to changes in the earth's magnetism. But these and other errors have been avoided in the apparatus to be described.

The source of radiation was a strip of heavy platinum foil, about 15^{mm} long and 1^{mm} wide, heated by a current of electricity. The experiments on the radiation from platinum were made from this wire direct, and those from the various other substances by coating the foil with the substances to be experimented upon; the heat generated by the current in the foil being sufficient to raise the substance to incandescence. The radiations from this wire were focused by means of a rock-salt lens, and dispersed by a rock-salt prism. A delicate thermopile was moved through the spectrum thus formed.

On the long table in the centre of the plate was a wooden box about seven feet long, and of the shape shown in the figure. This was intended to shield the experiment from outside radiations, and, besides being closed, was wrapped with woollen cloths during an experiment.

At S was placed the platinum wire, which was mounted between two brass rods, t' (Fig. 2). These rods were themselves mounted

in a vulcanite frame, and were connected, one with the battery direct and the other through the tangent galvanometer G , and the variable resistance R ; c was merely a commutator for reversing the current through the galvanometer; $w' w'$ (Fig. 1) are two exceedingly fine platinum wires welded to the main wire, about 8^{mm}. apart, and connected with a second galvanometer, G' . The object of these was to shunt off a small portion of the current, which, being compared with the main current, gave a method of determining the temperature of the large wire: this method will be further described.

The vulcanite frame was enclosed in a box of polished tin, shaped as shown in the figure. This peculiar shape was intended to reflect such rays as did not fall directly upon the lens to one side, and finally to the back, where they were absorbed by the ∇ shaped partition, behind which was a compartment filled with water.

The current for heating the wire came by means of the wires w , from a battery of thirty-two Bunsen cells, placed in the room below. It was measured by the galvanometer, G , placed on a stone pier, and its strength regulated by a mercury resistance, R .

The part of the current shunted off by the wires $w' w'$ was measured by a delicate galvanometer, G' , also placed on a stone pier. In this circuit there was a resistance of 1,000 ohms t , and a commutator c' for reversing the current through the galvanometer.

The rays that were given out by s passed through an opening, which could be closed, if desired, by the door of double tin, a , fell upon the rock-salt lens L and the rock-salt prism P , and produced a spectrum at $v b r$ about 15^{cm}. long. The lens and prism were both of perfectly transparent cloudless rock-salt. The lens was mounted in a double tube of brass, for focusing, the distance $S L$ being about 14 inches.

The prism was set on a plane surface, so as to be easily rotated or moved in any direction. It was set at its angle of minimum deviation by means of the reflection from the back, which, moving through twice the angle that the prism was moved, and over an arc whose radius was the distance from the prism to the pile, some four feet, furnished an excellent method of setting at the angle of minimum deviation for any part of the spectrum. After setting, this reflection was cut off by means of a little screen placed at the corner of the prism.

The thermopile T' was covered with camphor lamp-black, and enveloped, with the exception of the slit, by a double casing of tin. The back part of this was filled with water to absorb the extra rays, and to keep that face of the pile at a constant temperature. This screen,

with the enveloped pile, was fixed to a slide, $b d'$, so that it could be moved through the spectrum; the position of the pile being read off on a scale at d' . The tin case and pile also had a vertical motion, so that it could be raised and replaced by a simple slit, which was directly under the face of the pile. This slit was used in reducing the spectrum to that of the sun, by a method to be presently described.

Of course the heat radiated by the wire is very feeble, particularly after being dispersed by the prism, and we know that even the spectrum of the sun is not easy to measure. The ordinary short-coil Thomson galvanometer, when used with the pile, gave scarcely any deflection, even at the point of maximum heating effect of the spectrum, and in the luminous spectrum it gave no deflection at all.

Accordingly the Thomson galvanometer was modified as follows. The brass rod and magnet were removed, a hole made in the top, and a glass tube, about 25^{cm}. long, placed over this. Inside this was suspended an exceedingly fine silk thread, to the bottom of which was suspended the needle. It was necessary to form a suspension of this length, in order to eliminate the viscosity, which, even in a needle as delicate as the one used, was quite noticeable. The needle was made of eight small bars, about 8^{mm}. long, 1^{mm}. wide, and 1^{mm}. thick, placed four in the centre of the coil, and the other four, with poles reversed, below the coils. They were as nearly as possible in the same plane, and the system was found, when adjusted, to be so nearly astatic as to swing in fifteen seconds. The slight adjustment that was necessary was made by means of a small magnet, arranged so as to move in any plane, and placed at the side of the galvanometer at m .

This galvanometer was placed on a stone shelf at G'' , and its deflections read off by means of a scale and a spot of light at d . C'' was a commutator for reversing the current through the galvanometer. This galvanometer was, of course, exceedingly delicate; the passing of a finger by the pile was enough to throw the spot of light off the scale. It was exceedingly sensitive to changes in the earth's magnetism, so much so that on many days no observations could be taken at all. This, however, was avoided in general by reading on both sides of the 0 point of the scale, and by making the observations late in the evening, when the magnetic disturbances were at a minimum. Its sensitiveness, however, enabled the observer to detect the radiations of the violet part of the spectrum when the wire was heated to a white heat.

One great advantage of using so slight heating effects of the pile, and determining these by a low-resistance galvanometer, is that we

are much more certain that the galvanometer deflections are proportional to the heating effects.

Of course special precautions had to be taken to keep the lens and prism entirely free from moisture, a thin coating of which, such as would be deposited from the open air, would entirely vitiate the results. This was done by making the box one large desiccator, the bottom being covered completely with lead pans filled with pumice-stone and sulphuric acid, pans of these being clustered everywhere about the lens and prism. The lens and prism have now remained several months in the box with hardly an appreciable change.

Determination of Temperature.

I have described briefly the method of determining the temperature of the source of heat, but it still remains to describe the process more in detail, and to give the theory of the method. It was my intention, in beginning the experiments, to determine the temperature by measuring the variation of resistance of a platinum wire; but this particular arrangement of the apparatus was suggested to me by Professor Rowland.

We have seen that the current from the battery comes through the wire, which was rather a strip of platinum foil, then through the tangent galvanometer G , where it may be accurately measured, and then through the resistance R , where its strength is regulated. By setting up the cells, so that the internal resistance of the battery was very small, a constant current was easily obtained.

The two fine shunting-wires $w' w'$ took off an exceedingly small portion of this current, which was measured by the sensitive sine galvanometer G' . The theory of the method is as follows.

Let C = whole current from battery; C' , the current through the platinum wire; C'' , the current through the shunt. Let E, E', E'' be the corresponding electro-motive forces, and R, R', R'' the corresponding resistances.

$$\text{Then} \quad C' = C - C'' \quad E' = E'' = C'' R''$$

$$\text{and} \quad R' = \frac{E'}{C'} = \frac{C'' R''}{C - C''} = \frac{C'' R''}{C}$$

(since C'' is very small).

In general, for any value of the resistance of the platinum-wire,

$$R = \frac{k h \sin U R''}{K H \tan V} = R (1 + a t + b t^2 + \&c.)$$

Let R_i be the resistance at some known temperature t_i , and V_i and U_i the known corresponding deflections of the galvanometers, then

$$R_i = \frac{k h \sin U_i R''}{K H \tan V_i} = R_0 (1 + a t_i + b t_i^2 + \&c.)$$

For any resistance R_{ii} , we write in the same way :

$$R_{ii} = \frac{k h \sin U_{ii} R''}{K H \tan V_{ii}} = R_0 (1 + a t_{ii} + b t_{ii}^2 + \&c.)$$

From these two equations, by proportion,

$$R_0(1 + a t_{ii} + b t_{ii}^2 + \&c.) = \frac{k h \sin U_{ii} R''}{K H \tan V_{ii}} \frac{K H \tan V_i}{k h \sin U_i R''} R_0(1 + a t_i + b t_i^2 + \&c.)$$

or simply,

$$1 + a t_{ii} + b t_{ii}^2 + \&c. = \frac{\sin U_{ii} \tan V_i}{\tan V_{ii} \sin U_i} (1 + a t_i + b t_i^2 + \&c.)$$

If now we know the values of t_i and $\frac{\tan V_i}{\sin U_i}$ for any one case, and the coefficients a and b , we may, by simply reading U_{ii} and V_{ii} for any other current, determine the temperature from this equation.

As, for example, to determine t_{ii} we have merely to substitute the readings of the galvanometers U_{ii} and V_{ii} and solve relatively to t_{ii} .

The coefficients a and b have already been determined by Benoist,* viz.,

$$a = .002445 \qquad b = .000000572$$

To determine U_i and V_i for some temperature t_i , the wire was submerged in water at that temperature. This, of course, had to be repeated every time the wire was changed for a new one.

As may be seen upon examination, the theory of the method has nothing objectionable in it, and its practical accuracy depends upon the determination of the coefficients a and b . These were carefully determined by Benoist up to 860° C. For temperatures very much beyond this, as between 1,000 and 2,000 degrees, there is a liability to some error. But it is easily seen that the method is vastly superior to that of determining the temperature by the method of expansion.

Reduction to Sun's Spectrum and Determination of Wave-Lengths.

The image of the spectrum, as formed in the plane of the face of the pile, could be measured only in terms of divisions of the arbitrary scale attached to the slide on which the pile was placed. In order to determine the wave-lengths of the different parts of the spectrum for

* Phil. Mag., April, 1876.

which the thermal intensities were measured, it was compared with the sun's spectrum by the following method. The pile was made to slide up vertically so as to be replaced by the slit beneath it. This slit could then be moved to different parts of the spectrum, and its position read off on the same arbitrary scale as the thermopile. In fact, the readings for the two would be identical. Behind this slit was placed the slit of a single prism spectroscope, having a third tube and a photographed scale. As the pile was moved to different parts of the luminous spectrum an image of the slit beneath it was formed on the scale of the small spectroscope and its position could be read off in terms of the arbitrary scale.

A table was then formed containing in one column the readings of the thermopile scale, and in the second the corresponding readings of the spectroscope scale. Then the spectroscope was turned toward the sun and the positions of the principal Fraunhofer lines read off in terms of its scale. These readings formed a third column, and it was easy, by proper interpolation, to determine the position of these Fraunhofer lines in terms of the thermopile scale.

It now remained to determine the wave-lengths of these lines. This has already been done with great accuracy by Professor Powell,* and accordingly his values for these lines were made use of. The wave-lengths of the non-luminous portion were determined by means of empirical equations based on observations made in the luminous portion of the spectrum. Any considerable extension was, of course, accompanied with great error.

Some experiments with a diffraction grating are contemplated, and, if successful, will greatly help in determining the wave-lengths of the various parts of the curves here given. It must be remembered, however, that these experiments are principally of value in their relation to each other, and that the absolute determination of wave-length is therefore of only secondary importance.

Experiments with Platinum.

These experiments consisted of ten final and many other preliminary series of measurements of the distribution of heat in the spectrum of a platinum wire when heated to various measured temperatures between a low red and the point of fusion.

The method of experimenting was as follows. The vulcanite frame, containing the wire with its shunt, was first submerged in water of a known temperature, a faint current sent through it, and readings

* Pogg. Ann., lxix.

taken of the tangent and the sine galvanometers; this last being very sensitive, and the instrument used for measuring the small shunted current. This process was necessary every time a new wire was put in the frame, in order to obtain a constant that entered into the formula for determining the temperature. It was found necessary to change the radiating wire a great many times during the experiment, because of fusion by too strong a current.

The above process being completed, the vulcanite frame was set in position in the box, and a strong current sent through the wire so as to make a brilliant luminous spectrum. The pile was then raised so as to be replaced by the slit, the small spectroscopie placed behind this, and an exploration of the luminous spectrum made.

The pile was then lowered into position, the box carefully closed and covered with cloths, and left for several hours with the current cut off, so that everything in the interior might come to the same temperature. An even temperature being secured, sufficient current was sent through the wire to bring it to a low red heat, and the thermopile was moved step by step through the entire spectrum, and then back again; readings of the galvanometer being taken on both sides of the 0 at each step. The order of exploring the spectrum was sometimes reversed, sometimes the observations were begun at the middle and alternated, first to the right and then to the left, until the extremes were reached, and sometimes the order was from the extremes towards the middle. The method was thus varied in order to eliminate any possible error. The exciting current was kept constant during these measurements by means of the mercury resistance, and readings taken of both the tangent and sine galvanometers on both sides of the 0.

This series being completed, the temperature was varied and the experiment repeated; and so on for any number of temperatures, each series occupying from two to four hours' time. The results of the ten series are given in Table I., and are graphically represented by the curves of Plate II. These curves are each the mean of several observations, and are sometimes filled out in part from different series, all being reduced, of course, to the same ordinates and abscissas. Each curve has been constructed by plotting all the observations upon which it is founded, and drawing a mean curve through them. The number of series of measurements that entered into these curves was fifty-two.

The table shows the co-ordinates of the points of these mean curves. With each is given the temperature, and probable error of determination of a point near the *B* line. The points near the maximum were, of course, determined with far greater accuracy.

The experiment is one containing so many errors that it could not be expected that the experimental curves would be very accurate; but the large number of experiments made, on the other hand, give the mean curve probably with considerable accuracy.

An inspection of Plate II. shows us at once the important fact, that, though the temperature varies very considerably, the geometrical form remains very nearly, if not exactly, the same.

Of course it is quite possible that further and more delicate experiments may show slight variations in the form of this curve.

In fact, it is well known from the experiments of a large number of experimenters, and, indeed, from the change of color of the light as the temperature of a source of radiation is raised, that the geometrical form of the curve cannot be *entirely* independent of the temperature.

But such phenomena might easily be caused by variations too delicate to be detected by the thermopile.

TABLE I.

	OCT. 8.	NOV. 7.	SEPT. 27.	OCT. 9.	OCT. 8.	NOV. 7.	NOV. 6.	SEPT. 28.	OCT. 8.	NOV. 7.
	T = Faint red. p. e. = .07	T = 774° p. e. = .06	T = 870° p. e. = .09	T = 880° p. e. = .07	T = 880° p. e. = .04	T = 884° p. e. = .05	T = 795° p. e. = .06	T = 850° p. e. = .07	T = 1023° p. e. = .04	T = 1000° p. e. = .04
2		.06	.14	.18	.24	.30	.34	.36	.41	.45
2½										
3		.07	.17	.22	.27	.34	.38	.40	.47	.51
4	.02	.10	.19	.27	.31	.38	.42	.47	.57	.64
4½										
5	.03	.15	.24	.31	.35	.43	.48	.55	.83	.86
5½										
6	.06	.26	.40	.47	.47	.63	.68	.73	1.12	1.17
6½	.08	.37	.54	.67	.63	.78	.84	.89		
7	.15	.54	.76	.86	.82	1.07	1.14	1.21	2.35	2.48
7½	.31	1.02	1.51	1.67	1.57	1.95	1.84	2.09	3.98	4.36
8	.70	2.20	2.67	3.15	2.86	3.26	2.57	3.30	6.15	7.06
8½	.95	1.38	4.08	2.37	2.86	2.60	1.60	2.24	6.62	7.53
9	.48	.63	2.30	1.55	1.86	1.72	.69	1.53	4.50	5.12
9½	.28	.36	1.30	.95	1.17	1.08	.41	.95	1.92	2.10
10	.16	.26	.90	.65	.82	.77	.20	.73	1.43	1.56
10½	.09	.21	.74	.53	.67	.64	.12	.59		
11	.06	.16	.65	.45	.61	.56	.11	.50	.77	.84
11½										
12	.01	.10	.46	.31	.45	.40	.04	.35	.50	.56
12½										
13		.05	.35	.21	.32	.28	.03	.23	.40	.46
13½										
14		.04	.28	.15	.23	.21	.02	.20	.34	.38

B line 11.15

D line 12.45

E line 14.35

Experiments with Black Oxide of Copper (CuO).

The experiments with platinum having shown the curve of radiation to be independent of the temperature, it became desirable to see how it might be affected by using different substances as sources of radiation, and whether it is also true of other substances, that the form of the curve is independent of the temperature. Accordingly, the spectra from *five* different substances, varying widely in physical and chemical properties, have been measured, each at several different temperatures. The first of these was the black oxide of copper, CuO.

In order to obtain a long and narrow radiating source of this substance, the platinum wire was coated with a saturated solution of the nitrate of copper, applied by means of a camel's-hair brush, and then a current sent through the wire. The red fumes of nitric peroxide were driven off, leaving a coating of the black oxide, which became incandescent on further heating. Quite a thick coating was applied in order to make sure that the radiation came from the oxide, and not from the platinum.

These curves, the results of eighteen series of measurements, are given in Plate III. and Table II.

TABLE II.

	Red.	Bright Red.	White.		Red.	Bright Red.	White.
2	.09	.22	.47	9	1.31	3.26	6.81
2½	.10	.23		9½	1.00	2.61	5.19
3	.12	.24	.50	10	.83	2.09	4.07
3½	.12	.28	.55	10½	.68	1.61	3.27
4	.16	.32	.65	11	.52	1.23	2.49
4½	.20	.40	.80	11½	.41	.97	1.98
5	.24	.50	.96	12	.31	.67	1.45
5½	.34	.69	1.28	12½	.24	.55	1.17
6	.40	.83	2.62	13	.16	.44	.90
6½	.51	1.01	2.02	13½	.09	.33	.76
7	.66	1.37	2.73	14	.06	.26	.62
7½	.82	1.87	3.74	14½	.08	.23	.51
8	.98	2.51	5.00	15	.08	.19	.42
8½	1.20	3.20	6.29	15½	.09	.18	.39

B line 11.15

D line 12.45

E line 14.35

The lower curve represents the distribution at a low red heat, the second at a low white, and the third at a full white heat. In this last curve the radiating substance had melted and formed a black viscous

fluid, which still clung to the wire. It will be seen that the geometrical form of the curve is the same for all of the temperatures, and even when the substance has been converted into the liquid state. These curves are the graphically constructed means of the experimental curves, as in Plate II.

TABLE III.

	Al_2O_3 p. e. = .06	Cr_2O_3 p. e. = .07	CuO . p. e. = .05	Fe_3O_4 p. e. = .07	Pt. p. e. = .04
2	.05	.35	.43	.37	.47
$2\frac{1}{2}$.37	.45	.40	
3	.07	.42	.49	.46	.52
$3\frac{1}{2}$.47	.55	.49	
4	.09	.52	.64	.56	.74
$4\frac{1}{2}$.65	.80	.62	
5	.14	1.00	.99	.75	1.05
$5\frac{1}{2}$			1.28	.90	
6	.37	1.49	1.64	1.12	1.98
$6\frac{1}{2}$.82	2.52	2.10	1.57	
7	1.76	4.44	2.75	2.31	4.48
$7\frac{1}{2}$	3.13	5.73	3.75	3.95	6.50
8	6.79	6.97	5.00	5.94	6.64
$8\frac{1}{2}$	6.24	6.25	6.58	6.58	
9	2.38	4.66	6.50	4.47	3.06
$9\frac{1}{2}$.87	2.85	5.21	1.95	
10	.59	1.55	4.11	1.40	1.89
$10\frac{1}{2}$.94	3.31	1.06	
11	.40	.78	2.51	.75	1.00
$11\frac{1}{2}$.65	2.01	.60	
12	.32	.58	1.49	.48	.61
$12\frac{1}{2}$.54	1.21	.42	
13	.25	.50	.96	.39	.35
$13\frac{1}{2}$.46	.82	.34	
14	.16	.41	.68	.31	.26
$14\frac{1}{2}$.37	.58	.30	
15	.12	.34	.49	.30	.20
$15\frac{1}{2}$.30	.46	.30	

B line 11.23

D line 12.45

E line 13.86

The mean of the eighteen series of experiments is given also in Plate IV. and Table III.; all, of course, being reduced to the same value of the maximum ordinate. In fact, all of the curves of this plate are reduced in this way for convenience of comparison of their forms; their absolute size being unimportant, as no measurements of temperature were made except in the case of platinum. The curves are, of course, all reduced to the same sun spectrum, so that any of their parts are strictly comparable.

Experiments with Black Oxide of Iron (Fe_3O_4).

The wire was next coated with the black oxide of iron, which, though resembling in color the oxide of copper, is very different from it in chemical composition.

A solution of sulphate was applied with a brush, the volatile products being driven off by heating, and a coating of the Fe_3O_4 formed.

It was found that the form of the curve did not appear to vary with the temperature, and the mean of four careful series is given in Plate IV. and Table III., together with the probable error of determination of a point at the B line.

Experiments with Green Oxide of Chromium (Cr_2O_3).

The green oxide of chromium was prepared by coating the wire with chromic acid, and heating; the water was thus driven off and the higher oxides formed.

The resultant curve is shown in Plate IV. and in the accompanying table.

Experiments with White Oxide of Aluminium (Al_2O_3).

The wire was coated by applying a solution of ammonia alum, which, upon heating, was changed to Al_2O_3 , the other products being volatile. The substance thus formed was hard, vitreous, and pure white.

Nine series of experiments were made at several different temperatures to see that the form of the curve was the same. The mean result is given in Table III. and Plate IV.

It now remains to see what conclusions may be drawn from a study of these curves, and a comparison of them with each other.

The curves for platinum show very plainly, and those for the other substances confirm the conclusion, that the geometrical form is nearly independent of the temperature.

The study of the radiation from copper oxide enables us to extend this conclusion to the liquid state, so that we may conclude in general that *the distribution of heat in the spectrum of a solid or liquid source of radiation is nearly independent of the temperature of the source.*

Of course this conclusion can only be accepted within the limits that the accuracy of the experiments prescribes, and it must be admitted that further researches of greater delicacy may reveal slight variations in the form of the curve.

In comparing the spectra of the different bodies with each other, we wish to study the distribution of heat, and not the relative total emission. Accordingly, the curves of Plate IV. are all reduced to approximately the same size. An examination of this plate indicates a relation which further study may show to be of considerable importance, though the experiments thus far give hardly more than a hint of what the relation is.

If we regard each curve as an irregular triangle, and, starting from each of the angles, draw lines of symmetry toward the opposite sides, the point of intersection of these lines, or, if they do not intersect in a single point, the centre of the small triangle of intersection, may be regarded as a centre of area.

The wave-lengths of these several centres of area are found to be related to the molecular weights of the radiating substances.

They are not in exactly the same proportion, but, at least, they are in the same order, so that the greater molecular weights have the greater wave-length, and large or small intervals in one quantity are represented by large or small intervals in the other.

These results appear in Table V., in which the first column gives the substances, the second the molecular weights, and the third the wave-lengths of the centres of area. In the fourth column are given the abscissas of the point in the arbitrary scale adopted in the plates.

TABLE V.

SUBSTANCES.	Molecular Weights.	Wave-Lengths of Centres.	Positions of Centres.
CuO	79.4	.00096mm.	9.05
Al ₂ O ₃	102.8	.00107mm.	8.50
Cr ₂ O ₃	152.4	.00124mm.	8.10
Fe ₂ O ₃	160.0	.00126mm.	8.09
Pt	197.4	.00137mm.	8.04
Fe ₃ O ₄	232.0	.00145mm.	7.95

It would be useless to attempt the formation of an empirical equation connecting these quantities, as the experiments so far made are not sufficiently accurate to warrant it. In fact, in single observations the centres of area near together are sometimes reversed in order. Still, the mean curves point out a relation, which could hardly be accidental for all of the six substances.

The curves are all of so nearly the same form that the distances between even the extreme geometrical centres is not very great, and

thus exceedingly delicate experiments will be necessary to determine the exact relation. Still the intervals are very much larger than the probable error of the determination of a point, so that we may feel assured of the discovery of a relation which further experiments will perhaps determine quantitatively. And we must remember, as in the other experiments, that these measurements are very small and difficult to make; and the relation here indicated may prove, upon extensive examination, to have little or no scientific value. Further and more delicate experiments upon this point are, however, contemplated.

There is another relation between the curves of Plate IV. that is of considerable interest in its bearing on the theory of exchanges. If we compare first the curve of the black substance CuO and the white substance Al_2O_3 , we find the part of the former that corresponds to the luminous spectrum very much fuller than that of the latter; that is, the substance that absorbs nearly all the light rays at the ordinary temperature emits these rays most copiously when heated.

The green oxide of chromium, which is intermediate in color, and absorbs all but the green rays at the ordinary temperature, is also intermediate in its curve and emits least of all the green rays when heated. So the red oxide of iron is intermediate between the black and the green. But the curves also show us that we are not warranted in extending conclusions, drawn from observations of the luminous spectrum, to other parts.

In concluding this paper there is a strong temptation to speculate upon the meaning of the results obtained. That the geometrical form of the curve should be so nearly the same at all temperatures, and of the same *general* form for all substances, is a fact that probably must have an important physical interpretation. Does not the similarity of the curves for different substances show a similarity of movement of the ultimate components of the several substances, and so point to a similarity of ultimate composition of all matter, the slight differences in the grouping of these parts giving rise to the comparatively slight variations from the same form? Certainly this is not proof, but is it not evidence? And is it not probable that the superposition upon the radiations from the ultimate atoms, of the radiations from the groupings of these atoms, should cause the curve, as a whole, to move slightly to a shorter or longer wave-length, as the weight of a group is lighter or heavier? But I am aware that such speculations are founded on too insufficient data, and I offer these results merely as an experimental contribution to the science of radiant energy.